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13. ABSTRACT (Maximum 200 words)  Our experimental studies are directed at elucidating the mechanisms of interfacial adsorption, desorption, and reactions in collisions between chemical warfare simulants and solid surfaces. The investigations are facilitated by using molecular beam scattering from well characterized, MgO surfaces and model self-assembled monolayer or multilayer surfaces. Much of our efforts for this funding period have been focused on constructing a state-of-the-art ultrahigh vacuum gas-dosing instrument, synthesizing new MgO nano-structured materials, and exploring uptake in new silicon-oxide thin films. The instrument is now complete and enabling us to measure gas-surface reaction probabilities and branching ratios, determine surface adsorbate concentrations and structures, and measure the residence times and bonding energies of molecules on or within a material.			
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# Molecular Beam Studies of Reactions Between Warfare Agent Simulants and Solid Surfaces

## I. Novel MgO Sobant Surfaces and New Metal-Oxide Nanoparticles: Toward a molecular-level description of CWA chemistry on metal oxides

### I.A. Introduction

The primary challenge in developing materials for applications, such as protective coatings and decontamination, involves first developing a detailed understanding of the surface chemistry and then applying the understanding to build specific chemical structures tailored to achieve the desired outcome. During this funding period, we have focused our efforts on using our ultrahigh vacuum surface science techniques coupled with molecular beam dosing capabilities to develop a high-level understanding of how chemical warfare agent simulants react within a series of nano-structured metal oxide and silicon oxide materials. This section (Sect. I) focuses on our efforts to develop a new class of ultrahigh surface area MgO and explore decomposition and reactivity on this surface. In the following section (Sect. II), we review our key results associated with the reactions of simulants on specially-tailored silicon oxide thin films.

### I.B. Experimental Approach

The experimental approach for these studies involves using molecular beams to provide a source of simulants with precisely characterized chemical identity, approach geometry, and flux onto a particular surface sample. Reaction products that desorb from the surface are interrogated with a quadrupole mass spectrometer and the surface-bound products will be probed *in situ* with reflection-absorption infrared spectroscopy (RAIRS). The ultrahigh vacuum (UHV) environment isolates simulant-surface reactions from other processes, eliminates surface contamination, and allows the application of sensitive analytical techniques such as X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). Together with new surface preparation techniques, has been designed to reveal highly detailed insight into the molecule-surface interactions and help provide a strategy for developing novel materials.

The first year of funding on this project was dedicated toward the development of our ultrahigh vacuum surface analysis instrument. This instrument has been applied to create new ultrahigh surface area MgO surfaces and to explore the fundamental chemistry of simulants on this new material.

Table I outlines our approach and techniques for studying gas-surface reaction pathways. This approach is designed to address each of our overall research objectives, which are summarized in the lower portion of the table and discussed in detail in Sect. III.

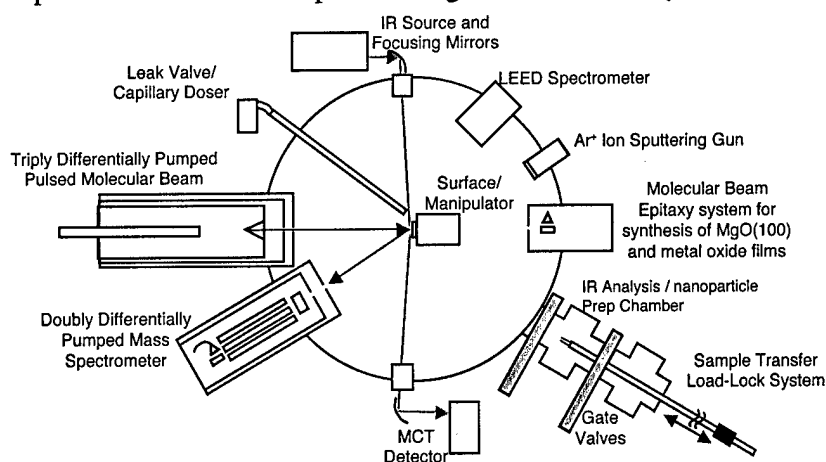
**Table I. Experimental approach and techniques designed to meet the specific research objectives.**

Experimental Approach	Experimental Technique	Sect.
create stable, well-characterized model surfaces	vacuum preparation of metal oxides	II.C
keep surfaces contaminate free during experiments	ultrahigh vacuum environment	II.B
characterize the surfaces	XPS and N <sub>2</sub> adsorptivity	II.B
control simulant flux and temperature	molecular beam exposure	II.D
isolate surface reactions from other processes	ultrahigh-vacuum environment	II.B
Research Objective	Experimental Technique	Sect.
measure uptake probabilities	King and Wells approach: beam and mass spec.	II.D
determine reaction pathways: gas phase products	King and Wells approach: beam and mass spec.	II.D
identify surface-bound products and structures	RAIRS (performed <i>in situ</i> ), XPS, and TPD	II.C
study the role of co-adsorbed solvent molecules	capillary doser and surface temperature control	II.B
determine the role of defect sites [on MgO(100)]	controlled argon ion bombardment and LEED	II. B

The schematic of our new beam machine is shown here. The experiments are performed in an ultrahigh vacuum surface-science chamber. The low background pressure ( $\sim 2 \times 10^{-10}$  Torr) ensures that: (1) neither contaminant background gases nor unwanted solvent effects contribute to the surface chemistry under investigation, (2) the surfaces remain clean and well-characterized throughout an experiment, and (3) several surface-sensitive analytical techniques can be implemented. The samples are mounted on a precision manipulator for temperature control and positioning. A load-lock system allows efficient sample introduction without venting.

An argon ion gun allows us to clean the surfaces through sputtering and annealing procedures and enable the creation of surface defects in a controlled manner. Reactant gas exposure is precisely controlled by entraining the molecules in a molecular beam with well-defined incident

translational energy. Creating the beams in a triply-differentially-pumped source chamber enables the flux of molecules at the surface to be varied over a wide range ( $10^{11} - 10^{15} \text{ cm}^{-2}\text{s}^{-1}$ ), while maintaining a low background pressure in the main reaction chamber, ensuring that reactions on the walls of the vacuum chamber do not interfere with the experimental studies. Furthermore, the collimated nature of molecular beams permits modulation of the beam intensity at frequencies as high as 400 Hz for time-dependent experiments. During beam exposure, products that form on the surface and desorb are monitored by a doubly-differentially-pumped quadrupole mass spectrometer,



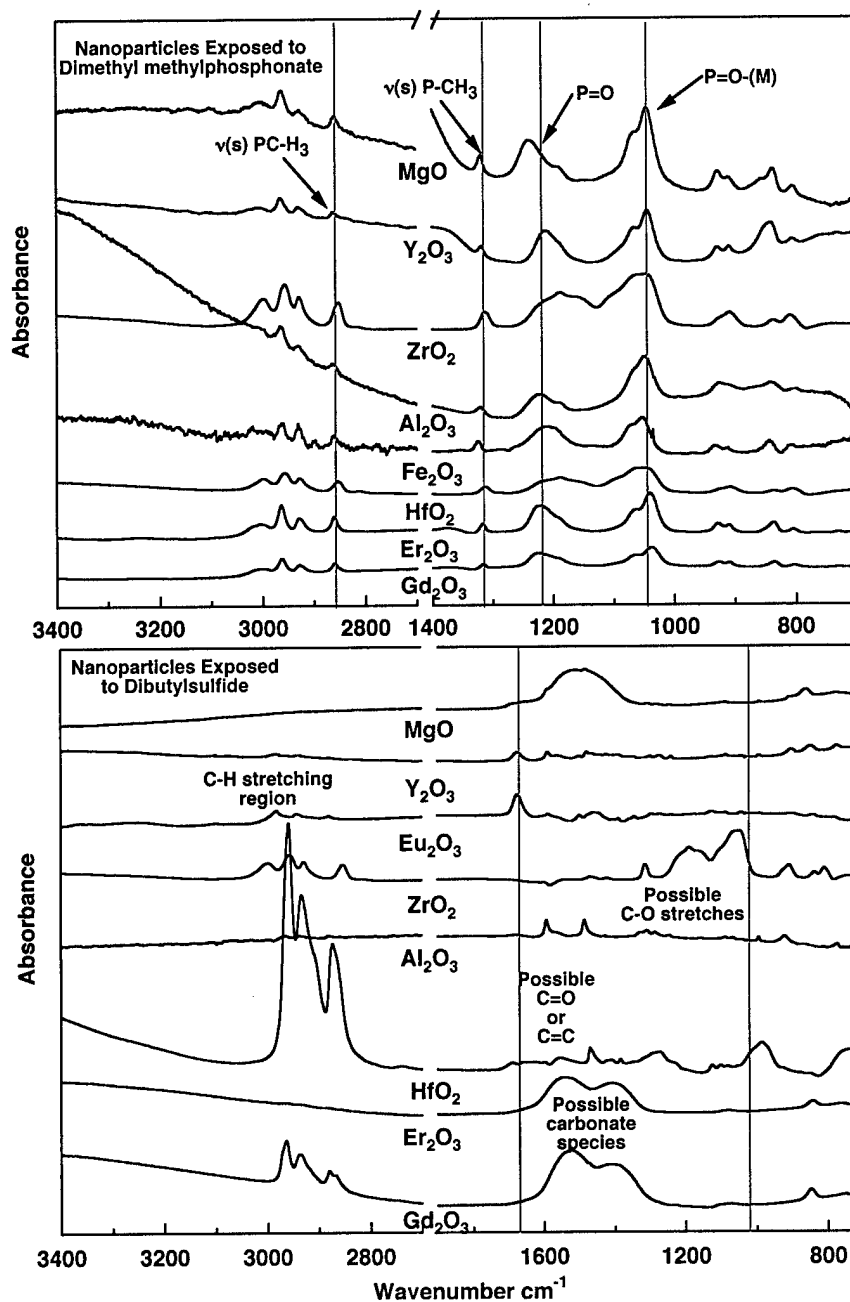
**Figure 1.** UHV molecular beam scattering and surface analysis apparatus for investigating the mechanisms of gas-surface reactions. Not shown is the X-ray photoelectron spectrometer.

while the surface-bound molecules are monitored with reflection-absorption infrared spectroscopy (RAIRS) using a mercury cadmium telluride (MCT) detector. This is one of only two such instruments in the world and the only designed specifically to explore CWA simulant-surface chemistry. This set-up was used both in the studies described here and in the studies described in Section II.

### **I.C. RAIRS study of simulant uptake on nanoparticles**

Our initial experiments have focused on studying the decomposition of CWA simulants on specially tailored metal oxide nanoparticles. Using the approach developed by Tissue *et. al.*, we have employed laser ablation techniques in the regulated atmosphere of a vacuum chamber to create a series of metal oxide films and nanoparticles.<sup>1,2</sup> The primary advantage of this technique over many other approaches for nanoparticle synthesis is that it affords control over particle size in an environment where the co-adsorption of background contaminants such as water and hydrocarbons is eliminated. Isolating the particles from ambient air affords fundamental studies into the role of water and hydrocarbon contamination on uptake and reactivity, a component of our future work. With this technique, we have synthesized a series of eight different metal oxide nanoparticles in the size range of 10-50 nm as determined by transmission electron micrograph (TEM) images. The particles were vapor deposited directly onto gold-coated glass substrates to provide a reflective surface for performing RAIRS to a probe simulant adsorption. For these initial studies, we have explored the uptake of the nerve agent simulant dimethyl methylphosphonate (DMMP), the chlorine-containing molecule 3-chlorophenol (3-CP), and the mustard simulant dibutyl sulfide (DBS). Although exposure levels were not precisely monitored for these initial measurements, we estimate exposures of  $\sim 10^4$  Langmuir for each gas. RAIR spectra were recorded prior to and subsequent to gas exposure and the difference spectra are shown in Fig. 2.

To our knowledge, these experiments represent the first studies into the reactivity of  $\text{Y}_2\text{O}_3$ ,  $\text{HfO}_2$ , and  $\text{GdO}_3$  nanoparticles with DMMP and DBS. For the organophosphonate, these experiments verify previous results showing that DMMP adsorbs primarily through non-dissociative molecular interactions, likely involving  $\text{P}=\text{O} \cdots \text{M}$  and  $\text{CH}_3\text{-O(-P)} \cdots \text{M}$  bonding on many of the metal oxide particles.<sup>3-7</sup> However, results for  $\text{HfO}_2$  and  $\text{ZrO}_2$  particles show strong evidence for dissociative adsorption with a  $\text{M-O-CH}_3$  symmetric stretch peak at  $2808\text{ cm}^{-1}$  (only a small peak on the scale of Fig. 2) and a significant shift and broadening of the  $\text{P}=\text{O}$  peak at  $\sim 1240\text{ cm}^{-1}$ .<sup>5</sup> These results are significant as they identify at least two nanoparticle systems for which dissociation of the simulant DMMP occurs at room temperature. A full analysis, including peak assignments and suggested mechanisms, will be presented in a forthcoming publication.



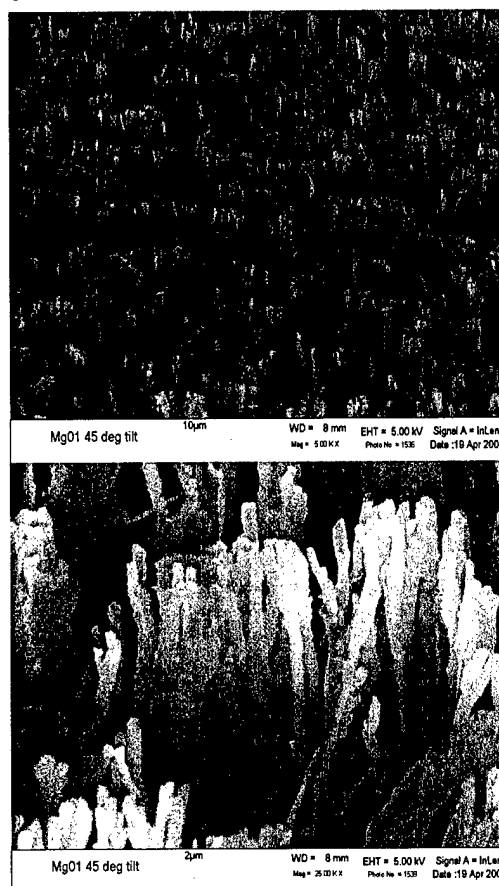
**Figure 2.** RAIR difference spectra for DMMP (top) and DBS (bottom) exposed to a series of nanoparticles created by laser ablation. The nanoparticles were vapor deposited on gold substrates to facilitate the reflection-absorption infrared measurements. Only the high-energy and low-energy regions of the spectra are shown in order to highlight the important peaks. The DMMP assignments come primarily from Ref. 12. The RAIR spectra for the DBS exposure are still unassigned and further studies are needed to help elucidate the chemical nature of the surface-bound products. Note: each spectrum has been scaled to facilitate plotting them all on a single graph.

The 3-chlorophenol exposure studies (spectra not shown) indicate that this molecule sticks well to each material studied, but adsorption is largely molecular in nature with little evidence for dissociation. In contrast, the chemistry is significantly different for the uptake of the dibutyl sulfide. This molecule exhibits different degrees of reactivity on every material studied. Evidence for large quantities of surface-bound products suggests that these materials may be highly effective catalysts for the decomposition of sulfur-containing agents such as VX and HD.

#### I.D. New ultrahigh surface area MgO: CWA uptake and reactivity

Recent experiments have demonstrated the ability to create highly porous (~90%), high-surface area (~1000 m<sup>2</sup>/g), thermally stable (1200 K) crystalline films of MgO using a reactive beam deposition (RBD) technique. Figure 4 shows an SEM image of a typical high-surface area film created with the RBD technique in our lab. We have perfected this technique to give us control over the surface area and overall morphology of the film. The film shown here, consist of a tilted array of porous nanoscale crystalline filaments. These films are presumed to have chemical binding sites analogous to those on nanoparticle materials. However, the fraction of chemically active high-energy binding sites is expected to be greatly enhanced on the nanoporous film.<sup>8</sup> Studies of the growth dynamics have been interesting. Our SEM investigations indicate that the surface is initially covered with a uniform distribution of MgO nanoparticles with a narrow size distribution and an average size of about 50 nm. Upon continued exposure past the nanoparticle phase, the filaments begin to grow. The lower image in Figure 4 shows some of the nanoparticles at the base of the filaments that were shadowed in some way from the magnesium oxide beam. The particles that are not shadowed grow into the long filaments.

With the successful implementation of the RBD technique in our group, we have embarked on a systematic study of CWA simulant uptake and reactivity. In particular we



**Figure 3.** SEM images of a nanoporous MgO film grown on oxidized Si(111) at room temperature and deposition angle of 85°. The filaments are tilted toward the direction of the incident Mg beam. The upper image is 40 μm X 40 μm and the lower image is the same film imaged at 10 μm X 10 μm.

aim to develop an understanding of how sticking probability and simulant decomposition depend on surface area, surface defect density, and morphology.

Initial results of the uptake probability of DMMP on the nano-filament surface depicted in figure 4 are shown in figure 5. The study shows that, when the DMMP molecular beam is turned on (150 s) the uptake is unity. The uptake decreases as the reactive sites become occupied with adsorbed DMMP and products, but it remains above 0.60 throughout the course of the measurement, until the beam is turned off (450 s). This measurement represents the first time that the absolute uptake probability has been determined for a CWA simulant on MgO. The very high uptake verifies the strong activity of this surface. The next question to address is whether the high uptake is due to decomposition or simple molecular sorption to this highly-porous material.

The reflection-absorption infrared results shown below provide some insight into the question of molecular decomposition on the new MgO materials.

The lower trace in each region of the IR spectrum shows clear evidence for significant uptake on the surface. The most exciting aspects of these spectra are: (1) the P=O mode is shifted significantly from the gas-phase spectrum, verifying that uptake occurs primarily through strong interactions between the P=O of DMMP and the surface MgO, and (2) a new band appears at  $1122\text{ cm}^{-1}$ , suggesting significant room-temperature decomposition of DMMP on the MgO surface. The decomposition product may be surface-bound  $\text{PO}_3$ . Temperature-programmed desorption studies are underway to verify this assignment.

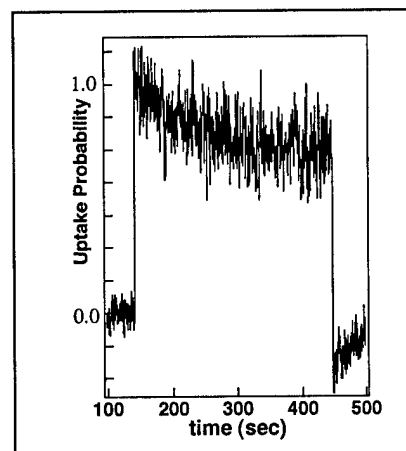


Figure 4. The uptake probability of DMMP on nano-filament MgO.

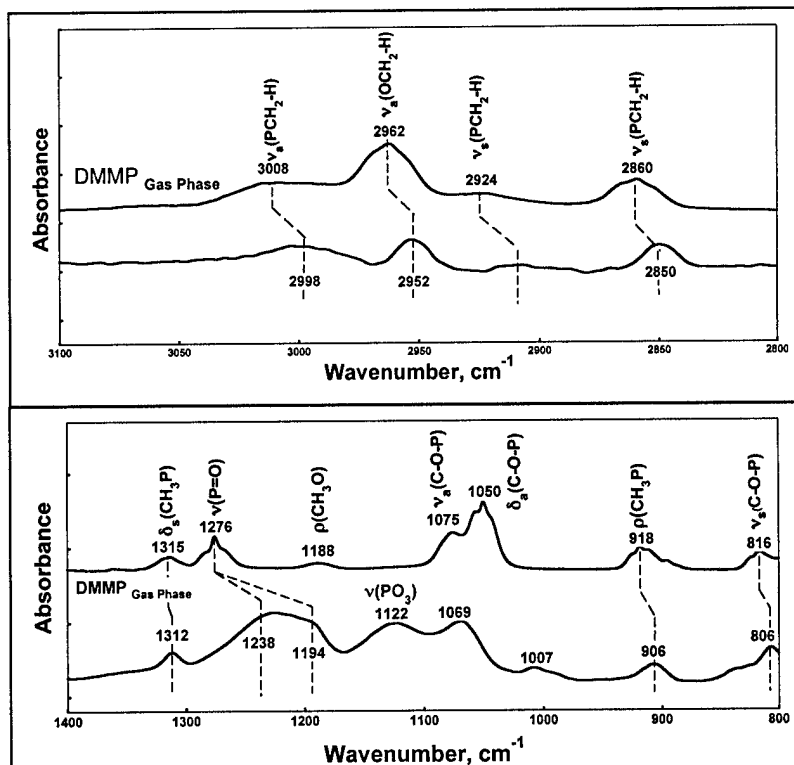


Figure 5. RARS study of DMMP uptake on nano-filament MgO. The upper figure shows the high-energy region of the spectrum and the figure on the bottom shows the low-energy region of the same spectrum. The top trace in each figure is the IR spectrum of pure gas-phase DMMP. The peak at  $1122\text{ cm}^{-1}$  may be due to the formation of surface bound  $\text{PO}_3$ .



## II. Uptake and Reactivity of Phosphorus Compounds within Langmuir-Blodgett Films of Trisilanolphenyl-Polyhedral Oligomeric Silsesquioxane

### II.A. Introduction

The development of efficient decontamination and sensing strategies for organophosphorus compounds has recently received much attention. The objective of this work is to continue the development and understanding of interaction pathways of the chemical warfare agent (CWA) simulants dimethyl methylphosphonate (DMMP), methyl dichlorophosphate (MDCP), and trichlorophosphate (TCP) on surfaces designed to sequester and decompose organophosphonates. The uptake and sorption characteristics of DMMP, MDCP and TCP on Langmuir-Blodgett (LB) films of trisilanolphenyl-polyhedral oligomeric silsesquioxane (POSS) are examined. As illustrated in the idealized schematic of Figure 1, the POSS films examined in the present study combine a silica core with hydrogen-bonding silanol groups and organic peripheral substituents.

### II.B. Uptake of Organophosphonates within POSS

Uptake coefficient measurements, conducted according to the King and Wells technique, indicate that the sticking probability of DMMP, MDCP and TCP on POSS films is below the detection limits of the ultra-high vacuum instrument used in this study,  $\sim 0.05$ .<sup>9</sup> The low uptake probability of the phosphate species within POSS is likely a consequence of the ordered, densely-packed, and hydrophobic nature of the outer surface of the POSS film.<sup>10</sup>

Despite a low uptake probability, under saturated vapor conditions at room temperature

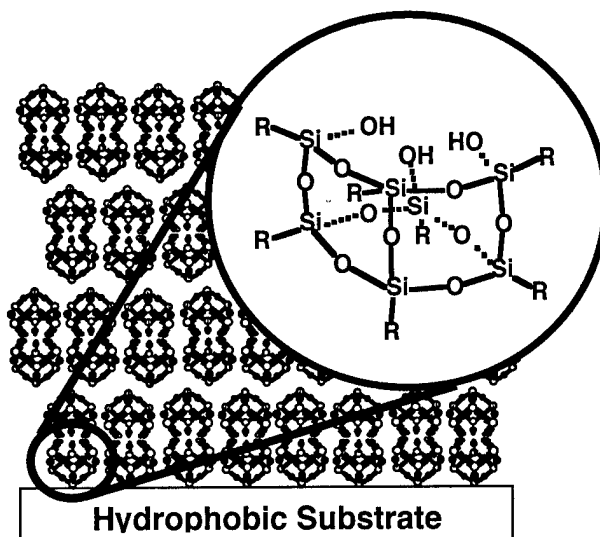


Figure 6. Using LB-film deposition techniques, POSS molecules are used to create well-ordered multilayer films that combine a silicon-oxide core with organic ring substituents and silanol groups. In this idealized schematic, R represents phenyl groups.

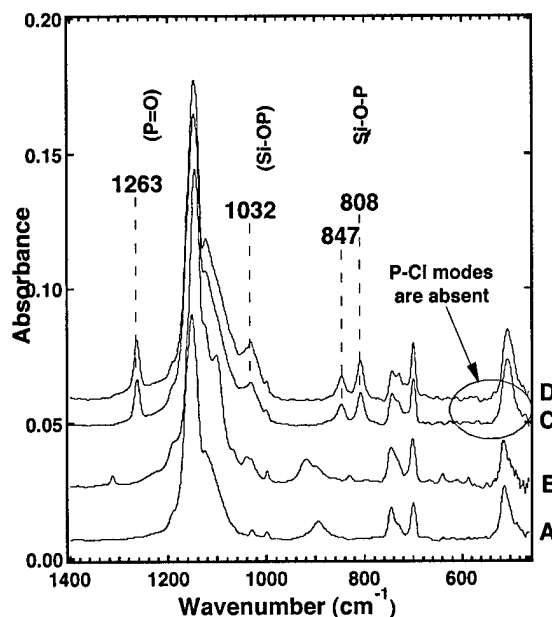


Figure 7. The RAIR spectrum of a freshly-prepared POSS LB-film (A) and the spectra of POSS LB-films saturated with DMMP (B), MDCP (C), and TCP (D). The presence of Si-O-P vibrational modes and the absence of P-Cl stretches denote a reaction between the chlorinated phosphate molecules and the POSS LB-films.

organophosphonate molecules are capable of diffusing into and adsorbing within the POSS films. Reflection absorption infrared spectroscopy (RAIRS) indicates that the significant quantities of adsorbed DMMP do not considerably disrupt the initial well-ordered film structure. Inspection of the high frequency modes (not shown) reveals a shift of the SiO-H mode from 3262 to 3380  $\text{cm}^{-1}$  upon sorption of DMMP. This shift is indicative of a disruption of the hydrogen-bonding network between silanol groups within the original POSS film.<sup>11-14</sup> The perturbation is likely the result of the formation of new hydrogen bonds between the silanol groups and the DMMP molecules.<sup>13,15</sup> In contrast, upon exposure to saturated MDCP or TCP vapor, there is a complete loss of the hydrogen-bonded SiO-H mode.

The low wavenumber IR data, shown in Figure 2, confirms weak interactions between the methoxy and methyl functional groups of the DMMP molecules and the silanol groups of the POSS films. Inspection of the phosphoryl stretching band reveals a significant shift from 1275  $\text{cm}^{-1}$  in the gas phase<sup>15-19</sup> to a broad shoulder positioned at 1234  $\text{cm}^{-1}$  in the DMMP-saturated POSS film. Examination of POSS LB-films saturated with the chlorinated phosphates, reveals a sharp, intense peak at 1263  $\text{cm}^{-1}$  in both spectra which is consistent with surface bound phosphoryl groups and a peak at 1032  $\text{cm}^{-1}$ , attributed to an Si-O stretching vibration in Si-O-P linkages.<sup>20,21</sup> Bands at 808 and 847  $\text{cm}^{-1}$  are likely associated with Si-O-P bending motions.<sup>20-22</sup> X-ray photoelectron spectroscopy (XPS) confirms the incorporation of phosphoryl groups within the POSS LB-film.

### II. C. Adsorption Energy of DMMP within POSS Films

Temperature programmed desorption (TPD) experiments were conducted to determine the adsorption energy of the DMMP molecules within the POSS film. Assuming zeroth order desorption kinetics and a pre-exponential factor of  $10^{13} \text{ s}^{-1}$ , a value of 122 ( $\pm 1.0$ ) kJ/mol is predicted for the adsorption energy of DMMP within a POSS film.<sup>23,24</sup>

### II. D. Mass Spectrometry

Bulk POSS and MDCP-exposed bulk POSS samples were subjected to fast atom bombardment-mass spectrometry (FAB-MS) to better characterize the reaction between the chlorinated phosphate species and the POSS molecules. In addition to the likely vapor-phase products, Scheme 1 shows the solid phase product that forms after the hydrolysis of MDCP molecules as

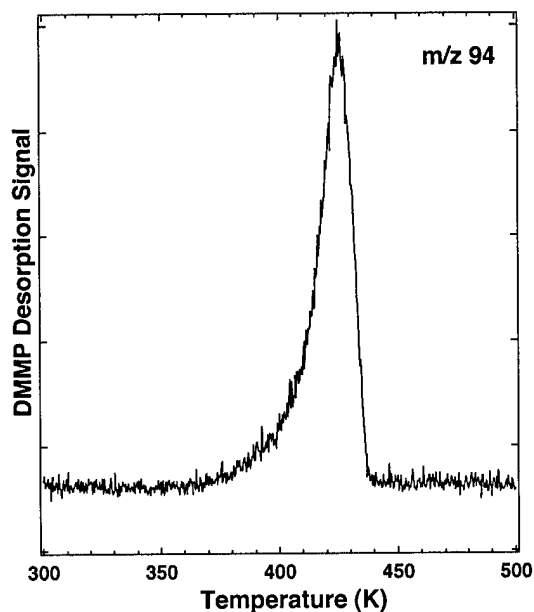


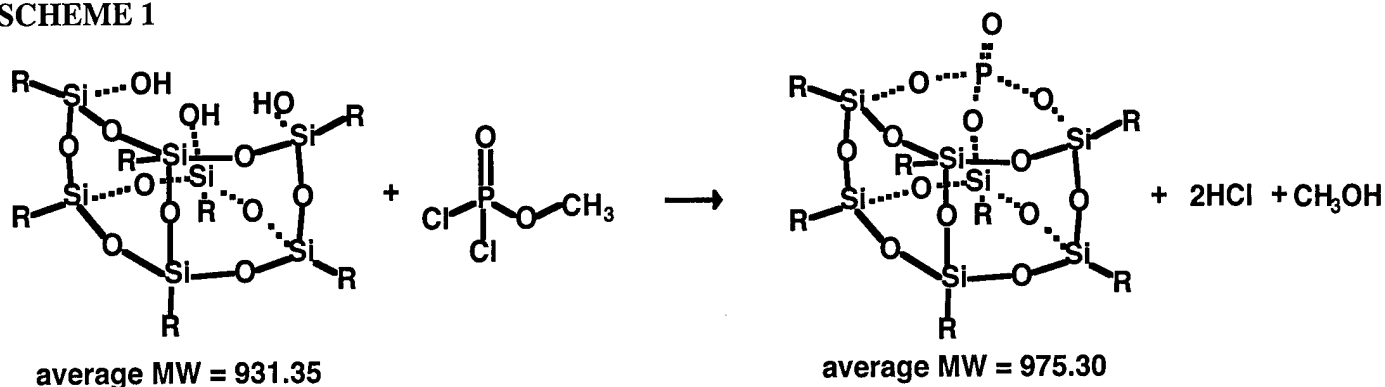
Figure 8. TPD of DMMP from a 40 layer POSS film. Shown is the trace of the m/z 94.

determined by FAB-MS analysis. A corner-capping reaction leaves a phosphoryl residue bound to a POSS molecule in bulk reactions. It is unclear whether the corner-capping reaction occurs in POSS LB-films or if a reaction with chlorinated-phosphate molecules results in cross-linking between neighboring POSS molecules.

## II. E. Section II Summary

The sorption of organophosphonates within a POSS LB-film was investigated by RAIRS, uptake coefficient, TPD measurements, XPS and FAB-MS. Even at very cold temperatures, the uptake probability of phosphate molecules on the ordered POSS films is very low. However, once the molecules penetrate the film, DMMP molecules hydrogen-bond with surface silanol groups and are held with an adsorption energy of 122 kJ/mol. MDCP and TCP react with surface silanol groups to yield phosphoryl functional groups incorporated with the POSS molecules.

SCHEME 1



### Publications from this work

#### Published

- (1) Shuler, S., Morris, J. R., "Energy Transfer in Rare Gas Collisions with Hydroxyl- and Methyl-Terminated Self-Assembled Monolayers," *Journal of Chemical Physics*, **116**, 9147-9150 (2002).
- (2) Ferguson, M. K., Low, E. R., Morris, J. R., "Well-Ordered Self-Assembled Monolayers with Buried Hydrogen-Bonding Functional Groups," *Langmuir*, **20**, 3319-3323 (2004).
- (3) A. R. Esker, B. A. Vastine, J. Deng, M. K. Ferguson, J. R. Morris, S. K. Satija, and B. D. Viers "Langmuir-Blodgett Films of POSS Derivatives," *Journal of the American Chemical Society Polymer Preprints*, **2004**, 45(1).

#### Submitted

- (4) Ferguson-McPherson, Melinda; Low, Emily R.; Esker, Alan R.; Morris, John R. "Uptake and Reactivity of Chlorinated Phosphorus Compounds within Langmuir-Blodgett Films of Trisilanolphenyl-Polyhedral Oligomeric Silsesquioxane" *Journal of Physical Chemistry B* (2004).

- (5) Ferguson-McPherson, Melinda; Low, Emily R.; Esker, Alan R.; Morris, John R. "Sorption of Dimethyl Methylphosphonate within Langmuir-Blodgett Films of Trisilanolphenyl-Polyhedral Oligomeric Silsesquioxane" *Journal of Physical Chemistry B* (2004).
- (6) Ni, Suolong; Lee, Woojin; Ferguson-McPherson, Melinda K.; Morris, John R.; Esker, Alan R. "Characterization of Highly Ordered Poly(L-Lactic Acid) Langmuir and Langmuir-Blodgett Films" *Macromolecules* (2004).
- (7) Deng, Jianjun; Ferguson-McPherson, Melinda K.; Morris, John R.; Esker, Alan R. "Characterization of Trisilanol-Phenyl Polyhedral Oligomeric Silsesquioxane Langmuir-Blodgett Films" *Langmuir* (2004).

#### ***Papers Presented at Meetings***

- (1) South-East Regional Meeting of the American Chemical Society, "Uptake and Reactivity of Chemical Warfare Agent Simulants on Nano-structured MgO" Ferguson, Melinda, and Morris, John R., Atlanta, Georgia, (2003).
- (2) Self-Decontaminating Materials and Multifunctional Coatings Workshop, "Uptake and Reactivity of Chemical Warfare Agent Simulants on Nano-structured MgO and SiO<sub>2</sub>" Ferguson, Melinda, and Morris, John R., Arlington, Virginia (2004).
- (3) American Chemical Society National Meeting, "Uptake and Reactivity of Nerve Agent Simulants on Nanostructured Silicon Oxide" Ferguson, Melinda, and Morris, John R., Philadelphia, Pennsylvania, (2004).
- (4) American Chemical Society national meeting, "Uptake and Reactivity of Nerve Agent Simulants on Nanostructured Silicon Oxide" Ferguson, Melinda, and Morris, John R., Philadelphia, Pennsylvania, (2004).
- (5) DECON 2004, "The Uptake and Reactivity of Simulants on Nano-structured SiO and MgO Thin Films" Morris, John R. Tampa, Florida (2004).

#### **Participating Scientific Personnel**

Caprice Hempley: Masters Degree (2002)

Melinda Ferguson: Ph.D. Candidate. (expected degree 2004)

Jeff Carter: Undergraduate Student (expected degree 2004)

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